

UNPUBLISHED PRELIMINARY DATA

EFFECTS OF HYDROSTATIC PRESSURE
CYCLING ON THE MECHANICAL BEHAVIOR
OF BODY CENTERED CUBIC REFRACTORY METALS
AND ALLOYS

(NASA Research Grant No. NsG-654)

INTERIM TECHNICAL REPORT No. 1
December 1964.

Submitted to:
Office of Grants and Research Contracts
Attention Code SC
National Aeronautics and Space Administration
Washington, D.C. 20546

GPO PRICE \$ _____

OTS PRICE(S) \$ _____

Hard copy (HC) 1.00

Microfiche (MF) .50

N 65 151 45

(ACCESSION NUMBER)

16

(PAGES)

CP 60177

(NASA CR OR TMX OR AD NUMBER)

(THRU)

1

(CODE)

17

(CATEGORY)

Department of Metallurgy
Case Institute of Technology
Cleveland, Ohio

ABSTRACT

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The effects of hydrostatic pressures of 5, 10, and 20 kilobars in inducing permanent changes in sub-structure have been investigated by transmission electron microscopy for a high purity iron and two iron-carbon alloys (0.065 and 0.30 weight percent carbon). The results show that after subjection to pressure, new dislocation arrays are found in the vicinity of many of the second phase particles present in these materials. These observations provide direct support for the hypothesis that the previously reported changes in the plastic behavior of iron-carbon alloys as the result of the application of hydrostatic pressure are due to the generation of 'free' dislocations.

Analogous studies on tungsten have been initiated. The structural changes on annealing rolled sheet of commercial purity are being followed to establish the nature of the fully annealed structure. Suitable techniques for the preparation of thin foils from 3/4" diameter tungsten bar are being developed. Preliminary pressure cycling experiments on annealed thoriated tungsten wire to peak pressures of 14 and 20 kilobars have been carried out.

Some aspects of the work on pressure-induced structural changes in iron have been accepted for publication in Physica Status Solidi.

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1. INTRODUCTION

In view of the potential importance of simple pressure cycling as a means of changing the plastic behavior of body centered cubic metals containing second-phase particles^(1,2) it is desirable to attain a better understanding of the nature and extent of these changes in various metals and of the structural factors controlling them. The current investigation was undertaken with the principal objectives of contributing to such an understanding by (a) attempting to verify a dislocation generation hypothesis proposed to account for the observed changes in mechanical behavior from transmission electron microscopy studies on pressure cycled iron and iron-carbon alloys, and (b) conducting some preliminary studies of pressure effects on substructure and plastic behavior in annealed tungsten - as a "brittle" body centered cubic metal - and molybdenum. The investigation was initiated on 1 June, 1964, and the present report describes the research carried out during the subsequent six-month period. While the principal effort in this period has been directed to the electron microscopy study of iron and iron-carbon alloys, useful progress has also been made in the analogous study of tungsten.

During the period 27 July - 8 August, 1964, the principal investigator, Professor S. Victor Radcliffe, was a guest of the Max-Planck Institut fur Metallforschung, Stuttgart, West Germany. In collaboration with Dr. H. Warlimont, the electromicroscopy study of foils of pressure-cycled iron and iron-carbon alloys was continued intensively during this period. Details of the results are included in the present report. A paper dealing with the pressure-induced changes observed in the substructure was presented orally at the Third European Electron Microscopy Conference in Prague (26 August - 2 September) and a more detailed account has been accepted for publication in Physica Status Solidi. 25 copies of the latter paper

have been submitted separately to the Office of Grants and Research Contracts, NASA.

Mr. G. Das joined the research program in September 1964 as a graduate assistant and has been concerned primarily with the work on tungsten.

2. EXPERIMENTAL WORK

(a) Effects of Pressure on Substructure in Iron-Carbon Alloys

It has been reported recently^(1,2) that the application of high hydrostatic pressures to annealed poly-crystalline iron-carbon alloys at room temperature can result in the elimination of discontinuous yielding and the depression of the flow stress on subsequent tensile straining at atmospheric pressure. Independently, the authors of both papers attributed these changes in mechanical behavior to the generation of dislocation at second-phase particles acting as elastic inhomogeneities in a matrix phase of isotropic linear compressibility. As the new dislocations would be formed at room temperature, "locking" by the migration of interstitial atoms to them would not occur readily. Consequently, they would be free to move on subsequent straining and give rise to the observed changes in flow characteristics. In support of this hypothesis, it has been shown that high purity iron does not exhibit such changes⁽²⁾, at least for pressures up to 10 kilobars, and that the effects diminish with increasing proportion of the second phase⁽¹⁾. In order to provide a more direct test of the hypothesis, the present study of pressure-induced structural changes by transmission electron microscopy was undertaken.

It is reasonable to expect that the nature of dislocation arrays developed from second-phase particles by the application of hydrostatic pressure would resemble the arrays of prismatic loops which have been observed in molybdenum⁽³⁾, for example, after a thermal cycle, and attributed

to stresses arising from the different thermal contraction of particle and matrix on cooling. Such stresses are analogous to those expected to arise under pressure from the different linear elastic compressibilities of the phases. The thermally developed arrays consisted of prismatic loops or helices moving on $\{011\}$ planes in $\langle 111 \rangle$ directions. The arrays were observed in transmission electron microscopy specimens only when the surface of the molybdenum foil was oriented close to a (011) plane - otherwise, the arrays apparently moved out of the foil during thinning.

Preliminary electron microscopy work in the present investigation on iron specimens prepared from rolled sheet material failed to provide clear evidence of new arrays of dislocations as the result of pressure cycling. The preferred orientation in annealed iron sheet is such that (100) planes are parallel to the rolled surface, i.e. (011) planes are at 45° and 90° to the sheet surface. In view of the reported orientation effect in molybdenum, it was concluded that the apparent absence of the expected new dislocations could be due to a similar effect in the iron. Accordingly, the subsequent work on iron and iron-carbon alloys has been carried out on sheet specimens cut from rolled bar in such a way as to maximize the probability of a set of (011) planes being parallel to the sheet surface.

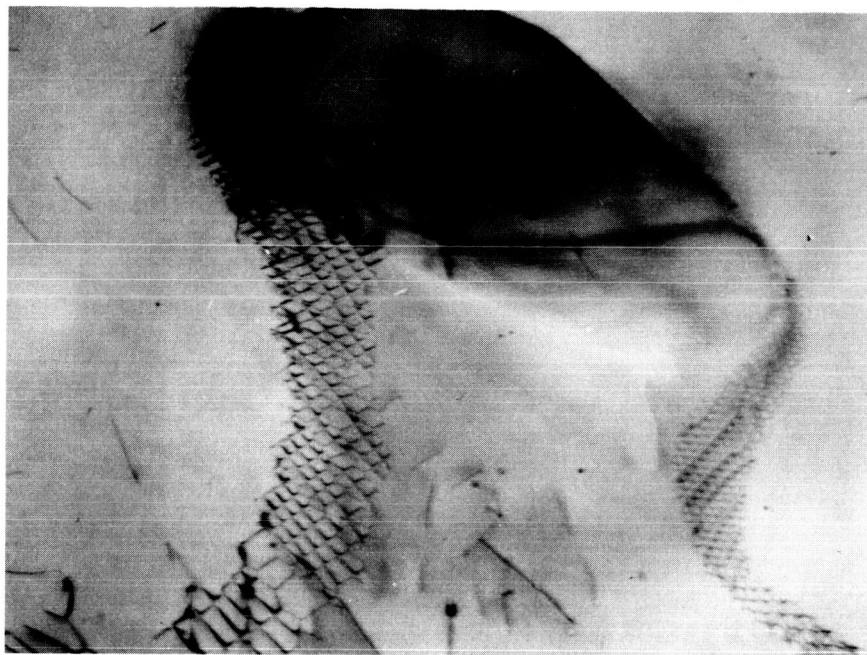
A high purity iron (0.004 wt% C) and three high purity iron-carbon alloys containing 0.065, 0.30 and 0.55 wt% C were obtained* in the form of 1 in. diameter hot-rolled round bar stock. Slices were milled at 90° and 45° to the bar axis and subsequently surface ground to give parallel faced sheets approximately 0.030 in. thick. These were then chemically thinned to 0.009 in. thick in a solution of 40 vol.% HNO_3 , 10 vol.% HF and 50 vol.% H_2O . This solution gives a high rate of thinning (approximately 0.010 in. per min.), but in the case of the two alloys highest in carbon the resulting surfaces were too rough for successful thinning to foils and had to be first

*Courtesy of U.S. Steel Research Center, Monroeville, Pa.

smoothed mechanically on silicon carbide papers. The sheets were then cut to dimensions suitable for foil preparation by the Bollman method. In addition, sets of 1/8 in. discs were punched from the sheets for foil preparation by the jet method.

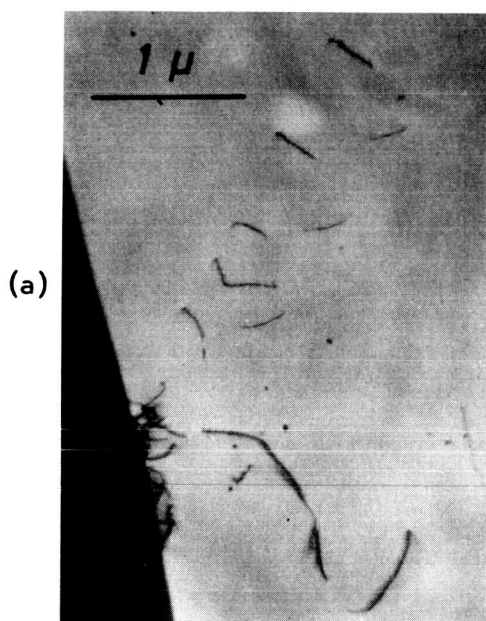
The initial microstructure of the three iron-carbon alloys consisted of regions of fine pearlite in a ferrite matrix. In order to provide a more uniform dispersion and a simpler morphology of the second phase (Fe_3C , cementite), experiments were carried out to determine a suitable spheroidizing heat treatment. Test samples were sealed in evacuated Vycor capsules, austenitised and isothermally transformed for long times at temperatures just below 727°C (the eutectoid temperature). The most satisfactory results from this type of treatment were obtained by the following sequence - austenitise at 927°C for 15 minutes, furnace cool to 695°C and hold for 17 hours, furnace cool to room temperature (8 hours). The sets of specimens for each alloy were sealed in separate Vycor capsules and subjected to this treatment.

Pressure cycling experiments to 5, 10 and 20 kilobars were carried out on batches of the heat-treated specimens including sheets and discs of each of the four compositions. In each case, a single cycle was used; the pressure was raised slowly (approximately 10-15 minutes per kilobar) held at the peak value for a few minutes, and released slowly (approximately 60 minutes). The 5 and 20 kilobar experiments were carried out with isopentane as the pressure transmitting medium in a piston-cylinder apparatus of 3/4 in. bore. The piston is driven by a 125 ton hydraulic ram. A 500 ton ram is used to effect closure of the other end of the cylinder and to develop constraining forces on the cylinder, which has a conical external shape, by driving it into a matching conical hole in a second larger cylinder. Pressure is monitored continuously by measuring the change in resistance of a manganin coil in the pressure chamber by means of an A.C. Bridge and chart recorder. The 10 kilobar experiment was carried out in a pressure bomb connected to an intensifier. The fluid used in this case was kerosene.



24,000 X

Fig. 1 - Example of dislocation arrays in carbide colony in as-annealed Fe - 0.3%C alloy.



(a)

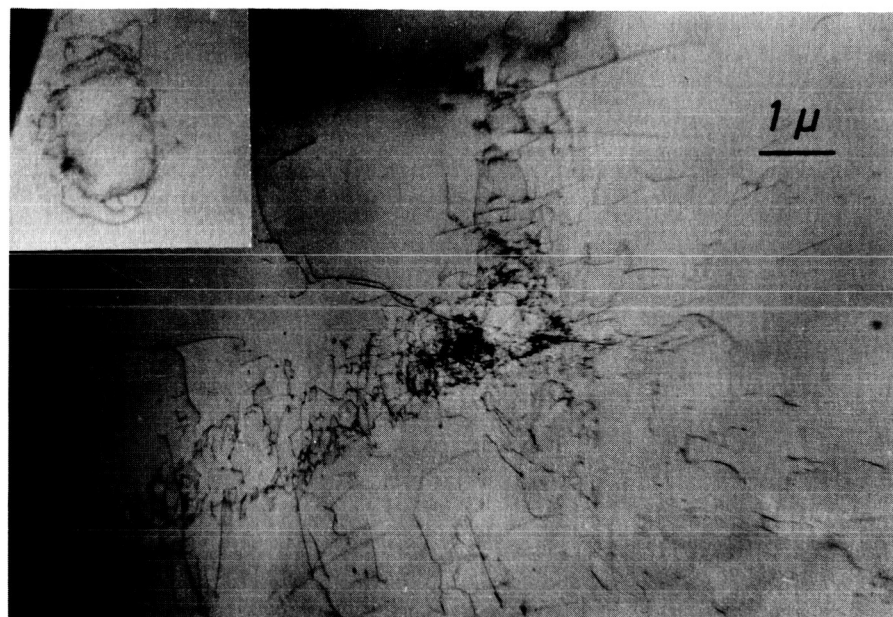
20,000 X



(b)

32,000 X

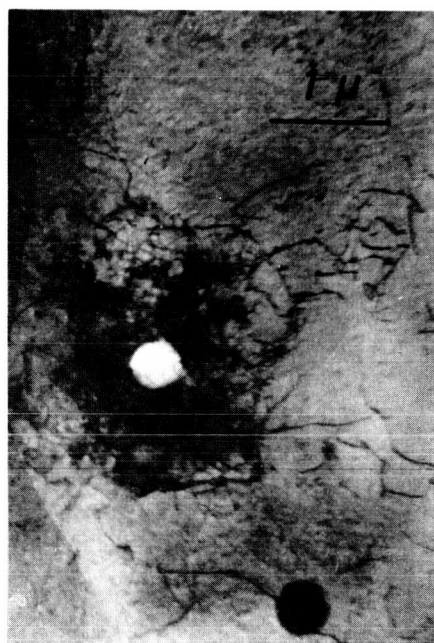
Fig. 2 - Examples of new dislocation arrays emanating from second-phase particles as the result of pressure treatment:
(a) Fe -0.065% C, 10 kilobars; (b) Fe- 0.3%C, 20 kilobars



10,000 X

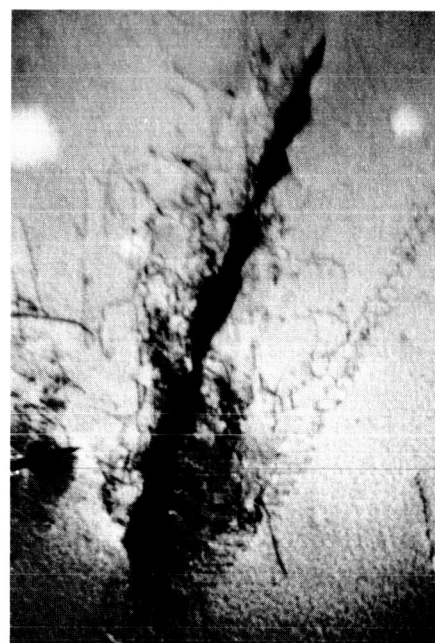
Fig. 3 - Dislocation tangles protruding from second phase particle. Insert shows dislocation ring which probably represents a cross section through such a protrusion. Fe - 0.3%C, 20 kilobars.

(a)



15,000 X

(b)



22,500 X

Fig.4 - Dense tangles of dislocations formed around a second-phase particle. (a) Fe -0.3% C, 20 kilobars, (b) high purity iron, 20 kilobars.

Foils for transmission electron microscopy were prepared from sheet specimens of both the as-spheroidised and the pressure treated material by chemical thinning (in a solution of 2 parts of orthophosphoric acid and 1 part of hydrogen peroxide at 70°- 90°C) followed by electrothinning by the Bollman method (in a solution of 135 cc acetic acid, 25 gm chromic oxide and 7 cc water at 8° to 16°C).

The microstructure of the specimens prior to pressure treatment consisted of large ferrite grains containing isolated carbide particles within the grains and at grain junctions, together with ferrite/carbide colonies. These colonies exhibited numerous stable dislocation networks as shown in Figure 1, whereas the large ferrite grains contained only a few isolated dislocations. In addition some unidentifiable inclusions were observed.

After subjection to pressure, additional dislocation arrays were found in the vicinity of many, but by no means all, second phase particles. The present analysis is restricted to dislocation arrays in the vicinity of isolated particles, since no conclusive observations could be made within the ferrite/carbide colonies because of the presence of complex dislocation networks there prior to pressure treatment.

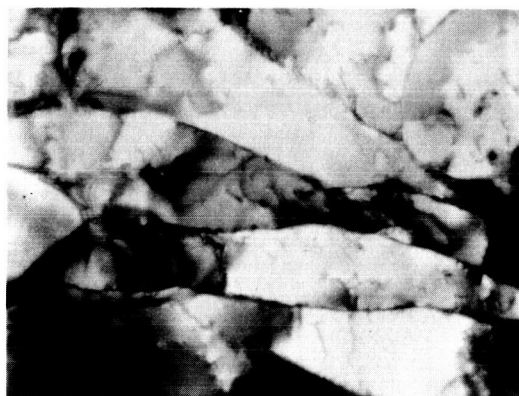
At the lower pressures applied (5 and 10 kilobars), the density of dislocations generated is low and the arrays resemble series of prismatic loops which have a common axis in well-defined crystallographic directions. Examples are shown in Figure 2a, where dislocations are seen to have originated from a particle located at the boundary of two ferrite grains, and Figure 2b, where a helix-like array is emanating from a larger particle.

At the highest pressure applied (20 kilobars), two main types of more dense and complex dislocation arrays develop. In the first type, dislocation tangles protrude from a particle in specific directions to distances large compared to the particle diameter, as shown in Figure 3. Dislocation

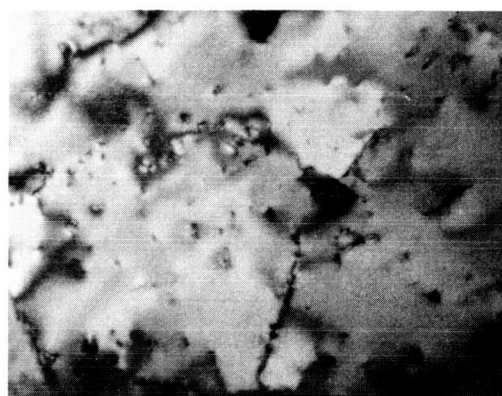


(a)

50,000 X



20,000 X



20,000 X



20,000 X

Fig. 5 - Substructure in tungsten sheet. (a) as-rolled condition, (b), (c) and (d) vacuum annealed at 1180°C for 10 minutes.

arrays like that shown in the insert of Figure 3, which was taken from a different area of the same specimen, were observed occasionally and probably represent cross sections through a protrusion. The second type consists of a very dense tangle surrounding a particle, with its dislocation density decreasing uniformly in directions away from the particle-matrix interface. An example is given for a spherical particle in Figure 4a. In the case of the high-purity iron, occasional long and thin particles were observed in the foils. They could not be identified by electron diffraction, but did give rise to dislocation arrays of the second type - as shown in Figure 4b.

These observations provide direct support for the hypothesis that the reported changes in the plastic behavior of iron^(1,2) are due to the generation of dislocations during the pressure cycle. Arrays of the kind shown in Figures 2 and 3 suggest, more specifically, that prismatic punching⁴ is one of the operating mechanisms of dislocation generation. The pressure-induced arrays are analogous with, but more complex than, those formed by thermal contraction stresses at second-phase particles on cooling.

It is not clear from the present work why dislocations are not observed at all isolated carbide particles after pressure treatment. However, there is some evidence that the dislocations appear more frequently at the larger and/or more asymmetric particles. A greater proportion of the occasional inclusions observed in the alloy foils exhibited dislocation arrays than did the carbide particles. This indicates a smaller linear compressibility or larger anisotropy for the inclusion. Lack of relevant elasticity data precludes verification of this point.

(b) Effects of Pressure on Substructure in Tungsten

No previous studies of the effects of pressure cycling have been reported for tungsten. However, it was anticipated that for annealed powder metallurgy material of commercial purity, or with deliberate small additions

of a second phase, e.g. thoria, subjection to a pressure cycle should lower the flow stress in an analogous manner to the effect in iron. In the case of the tungsten, this could lead to a lowering of the transition temperature from ductile to brittle behavior which might be sufficient to improve its room temperature ductility.

The initial efforts in the present investigation have been directed to developing suitable techniques for the preparation of foils for electron microscopy, to establishing appropriate annealing procedures and examining the structures developed in the annealed material. In addition, some preliminary observations are being made of the effects of pressure cycling on the mechanical behavior of annealed thoriated tungsten (2% thoria) wire.

In view of the effects of preferred orientation experienced with iron, tungsten in the form of sintered and extruded rod 3/4 in. diameter, was selected for the pressure study. Sample rods made from 99.99% W powder stock and prepared in the undoped and doped conditions and with 2% thoria addition have been obtained. After observation of their annealed structures, one of these materials will be used for main study. Because of the difficulty of machining tungsten by normal methods, the technique adopted for preparing foil specimens consists in high voltage spark-machining a 0.030 in. thick slice from the bar stock, and spark-planing the slice to 0.015 - 0.020 in. thick. The slice is then electropolished to foil by the window and Bollman methods used in succession. Attempts to apply this sequence directly to annealed undoped tungsten (annealed in vacuum at 1675°C for 15 min.) have not yet provided satisfactory foils. The principal problem encountered has been the need to mechanically polish the planed specimens to smooth the surfaces before electropolishing. Without such smoothing, general perforation occurs before the foil is thin enough for electron transmission. However, the extreme brittleness of the annealed tungsten makes it difficult to avoid cracking during mechanical polishing; such cracks also lead to

early perforation during subsequent electropolishing. Attempts to overcome these problems are being made by (a) improving the method of mechanical polishing and (b) carrying out the slicing, planing and mechanical polishing operations on as-extruded tungsten, which is less brittle.

In order to gain experience in the transmission electron microscopy analysis of tungsten at the same time as developing the specimen preparation method for bar stock, foils have been prepared from undoped tungsten in the form of 0.006 in. thick rolled sheet. The technique adopted for the sheet consists in chemically polishing in a solution containing 35 cc HF, 35 cc H_2SO_4 , 50 cc HNO_3 and 50 cc H_2O at $100^{\circ}C$ to reduce the thickness to approximately 0.002 in., followed by electropolishing in a 2% NaOH solution at room temperature using the window and Bollman techniques in succession. Considerable improvement in the quality of polishing was achieved by the use of a battery voltage supply rather than the usual rectified A.C. supply, and by careful control of the stirring of the electrolyte.

Some of the structures observed in as-rolled and annealed sheet are shown in Figure 4. The as-rolled sheet (Figure 4a) consists of elongated sub-grains with containing dense dislocation tangles and some evidence of a cell structure. After vacuum annealing at $1180^{\circ}C$ for 10 minutes, the greater part of the specimens examined exhibited larger grains containing isolated dislocations and a polygonised substructure (Figures 4c and 4d). Some areas still exhibit elongated subgrains (Figure 4b) with their long axis close to the $[011]$ direction, the preferred orientation in tungsten sheet, but the density of dislocations in them is considerably less than in the as-rolled material. Further annealing experiments are in progress with the tungsten sheet in order to establish clearly the structural characteristics of the fully annealed material, including the presence and distribution of any second-phase particles.

To effect some preliminary observations of the effects of pressure cycling on the mechanical behavior of tungsten prior to the selection of the material for detailed study, experiments have been conducted on 0.030 in. diameter wires of thoriated tungsten. Straight specimens, 4 in. long, were vacuum annealed at 1300°C for 10 minutes and then pressure cycled in a similar manner to the iron specimens to peak pressures of 14.5 and 20 kilobars. Attempts to carry out tensile tests in a constant strain-rate machine (Instron) have as yet been unsuccessful due to premature fracture in the grips. Variations in grip design and electropolishing a reduced section on the central length of the test specimens have not overcome this difficulty. Although simple bend tests appear to indicate some improvement in strain to fracture, no clear conclusion of the effect of pressure on this material can yet be deduced. The fact that the as-drawn material can be tested successfully indicates that any such effect is small. As shown by the earlier results for iron-carbon alloys⁽¹⁾, increasing amounts of second phase can eliminate pressure effects on flow stress, and this may be the reason for the results obtained for the tungsten - 2% thoria alloy. Further tests have been initiated on unthoriated tungsten wire.

3. FUTURE WORK

During the next six-month period of the program, further attention will be paid to the effect in iron-carbon alloys of the volume properties of the second phase and the magnitude of the applied hydrostatic pressure on the nature of the changes in substructure. Tensile stress-strain measurements will be correlated with the structural observations and the effects of aging will be examined. In the case of tungsten, the electron microscopy study of the annealed structure will be completed on the sheet material and extended to the various rod materials. The effects of pressure cycling on the selected material will then be examined with respect to electron microstructure and tensile behavior at room temperature. Depending on the nature of the results obtained for tungsten, a limited study will be conducted of the effects of pressure cycling on molybdenum.

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